

X-RAY STUDY OF SO CALLED AMORPHOUS VARIETIES OF SILICA

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY
STUDIES OF THE JOHNS HOPKINS UNIVERSITY
IN CONFORMITY WITH THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

By
ISADOR LEVIN

BALTIMORE, 1932

Reprinted from
ZEITSCHRIFT FÜR KRISTALLOGRAPHIE
Bd. 85, Heft 3/4, 1933

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Acknowledgement.

The author is most grateful to his parents for making his university work possible. He is indebted to the entire Chemistry Staff for instruction and guidance in laboratory and classroom. He wishes especially to thank Dr. Emil Ott for his aid and advice throughout the research and Professor Walter A. Patrick for his helpful instruction during the early stages of the work. Dr. E. G. Zies and Dr. C. N. Fenner of the Geophysical Laboratory in Washington very obligingly supplied samples of two modifications of silica. Dr. E. P. Henderson of the U. S. National Museum assisted greatly by supplying specimens and making optical examinations of a large number of opals from the collection of that museum.



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X-Ray Study of Opals, Silica Glass and Silica Gel¹).

By

I. Levin and Emil Ott in Baltimore.

(With 6 figures.)

A. Study of Opals.

Introduction. On the basis of optical examinations opals have for long been considered as outstanding examples of truly amorphous solids.

The introduction of structure determination by means of X-rays did not add anything essentially new in this field as may be judged by the following review of previous work.

Rinne²) finds that the opals examined (hydrophane, milkopal, hyalite from Walsch, and kieselguhr), gave patterns with two broad interference bands. Note that this is the type of pattern obtained from liquids.

Kerr³), states that a number of so called amorphous materials were examined but that opal was the only one that gave no lines.

W. M. Lehmann⁴) reports that common opal and precious opal gave faint traces of diffraction lines in the vicinity of the primary spot, and that fireopal gives already a few weak interferences and the hyalite examined gives distinct quartz lines. He concludes with the statement that common opal and fireopal are, as formerly, to be considered as amorphous.

H. Heinz⁵), working with mixtures of chalcedony and opal, establishes the existence only of quartz lines on his photographs.

1) From a thesis entitled: "X-ray study of so called amorphous varieties of silica", submitted by I. Levin in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

2) Rinne, Z. Krist. **60**, 55. 1924.

3) Kerr, Econ. Geology **19**, 1. 1924.

4) W. M. Lehmann, Z. Krist. **59**, 455. 1924.

5) H. Heinz, Chemie der Erde **4**, 501. 1930.

E. Baier¹⁾ in a long article "Die Optik der Edelopale" makes the following statement on page 249 "Bei der Röntgenuntersuchung machten sich kristallisierte Bestandteile nicht bemerkbar". (No crystallized components were made observable by X-ray examination.)

Since chalcedony (essentially micro fibrous quartz) frequently occurs together with opal, one naturally expects the appearance of the quartz pattern with an occasional sample of opal. Therefore, the above reports added little to the results already obtained by optical examination.

X-ray Results obtained in this Work²⁾.

Contrary to what would be expected from the results reported in the literature, many of the opals (hyalite and geyserite will be included in the second part) gave patterns consisting of many fairly sharp lines; which is characteristic of the presence of crystalline material. The remarkable fact is that most of these gave an identical pattern fitting none of the patterns of the three modifications of silica which according to Sosman³⁾ have been found to exist at room temperature. This pattern was finally identified as that of high cristobalite. The simplicity of the pattern suggested that it belonged to a cubic substance. Certain similarities with the low cristobalite pattern, together with the fact that high cristobalite was reported to be cubic, caused us to compare the line measurements with those for high cristobalite reported by Wyckoff⁴⁾. Within the limit of accuracy of our measurements, excellent agreement was found for spacings and relative intensities. To make the identification perfectly convincing, photographs of high cristobalite were prepared by exposing to the X-ray beam a rod of cristobalite powder kept above the inversion temperature.

1. The four types of patterns.

Before giving the X-ray photographs and measurements, the results obtained will be summarized. The patterns obtained divided the opals into four groups.

1. Those showing the lines of high cristobalite only.

1) E. Baier, Z. Krist. **81**, 183. 1932.

2) Compare our preliminary note, I. Levin and Emil Ott, J. Am. chem. Soc. **54**, 828. 1932.

3) Sosman (1927) "Properties of Silica", J. Am. chem. Soc. Monograph No. 37, Chemical Catalog Co.

4) Wyckoff, Am. J. Sci. **9**, 448. 1922.

a) U. S. National Museum No. 82566¹). A slightly translucent, slightly yellowish brown sample from Queretaro, Mexico. The optical examination showed, "grains are almost clear. No doubly refracting material present. Index of refraction 1.418—1.422."

b) U. S. National Museum No. 48095. A hard dark brown wood opal. Analysed 3.7% volatile matter, 0.10% non volatile impurity. Optical examination: "Grains all show a woody texture. Almost no doubly refracting material present. Most of the grains have refractive index below 1.42. Refractive index 1.415—1.423."

c) U. S. National Museum No. 95752. A slightly yellowish milky sample from Humboldt County, Nevada. Analysed 0.60% non volatile impurity. Optical examination: "Grains are cloudy but no doubly refracting material is present. Refractive index 1.414."

d) No. 1 from the Geology Department of the Johns Hopkins University. A white, slightly milky sample of unknown origin.

e) No. 2 from the Geology Department. A slightly reddish yellow, almost completely transparent sample of unknown origin.

f) No. 3 from the Geology Department. An iridescent sample of unknown origin.

2. Samples showing the lines of quartz and of cristobalite. It cannot be said at present whether the cristobalite was present as high cristobalite, low cristobalite, or a mixture of the two.

a) National Museum No. 81178. A white slightly milky sample from Camp Verde, Arizona. Optical examination: "Grains are cloudy and contain inclusions of doubly refracting material. Refractive Index 1.448."

b) National Museum No. 93818. Fine soft dark gray fibers. Sample from Esmeraldo County, Missouri. Optical examination: "Fibrous or prismatic material, some of which are doubly refracting. A few of the fibers have a refractive index of over 1.475. Refractive index 1.416—1.422".

3. Sample showing lines of both low and high cristobalite. U. S. National Museum No. 16438. A colorless, very slightly milky sample. Optical examination: "Clear. Index of refraction 1.425".

Examples of some types of line pattern are reproduced and placed next to patterns of the standards so as to show the identities.

1) All of the samples from the U. S. National Museum, Washington, D. C., were obtained through the courtesy of Dr. E. P. Henderson, who also made the optical examinations reported.

The quartz standard was a small clear quartz crystal obtained from the collection of the Geology Department. The tridymite (No. 106) was prepared by heating quartz and sodium tungstate to 1000° for seventy-one hours. The cristobalite (No. 108)¹) was prepared by heating finely ground purified quartz with sodium tungstate at 1590° .

During the exposure of the contact prints the lighter portions of the negatives were shaded.



Fig. 1. Opal, Nat. Museum, No. 82566.



Fig. 2. High Cristobalite, 450° .



Fig. 3. Opal, Nat. Museum, No. 16438.



Fig. 4. Low Cristobalite.

X-Ray technique.

Three cylindrical "powder" cameras of essentially Scherrer's design were used. No. I has an effective circumference of $180/.990$ mm.; II and III have an effective circumference of $180/.994$ mm. All three are of

¹) These samples of tridymite and cristobalite were obtained through the courtesy of Dr. C. N. Fenner and Dr. E. G. Zies of the Geophysical Laboratory in Washington, D.C.

such construction that the primary beam passes through the camera without any chance to be scattered or reflected into the film except by the sample. In place of black paper for the light shield through which the X-ray reflections reach the film, 0.02 mm. aluminum foil was used. In addition to keeping out the visible light, the aluminum foil serves to absorb soft fluorescent radiation coming from the irradiated sample.

For all the photographs, copper radiation from a Hadding gas tube or Seemann hot filament tube was used, generally after passing through a nickel foil of sufficient thickness (0.02 mm.) to make β radiation undetectable.

Since it was found that excessive tube voltages resulted in bad fogging, the tubes were finally run at the lowest voltages that gave good intensity: about thirty kilovolts effective with the Hadding tube and about twenty kilovolts effective with the Seemann tube. With the latter tube, practically complete freedom from tungsten or mercury radiation was assured by examination with a spectrograph, using a calcite crystal.

Eastman duplitized X-ray film was used for all exposures.

In the study of fused silica where it was desired to use the copper $K\alpha$ -doublet essentially free of continuous radiation, the regular slit system of camera III was replaced by a Seemann rocksalt monochromator.

All grinding of samples was done with a well cleaned agate mortar and pestle. Since agate is essentially crystalline quartz, any contamination by the mortar could interfere only by producing the stronger lines of quartz on the photograph. All of the materials photographed, originally known not to contain quartz, showed no trace of a quartz line despite the fact that some of these were very hard materials and were ground for over an hour. It is, therefore, reasonably certain that any material which showed quartz lines of high or moderate intensity, contained quartz before grinding.

The appropriately powdered sample was shaped into a cylinder in one of two ways. The first method is to pack the powder into thin walled tubes made of collodion. The collodion gives no crystal lines but does give some bands and diffuse diffraction. It, therefore, causes no interference in the qualitative study of any crystalline materials. Accordingly, the first sample of a material was prepared this way.

If the resulting photograph was not of the crystalline type, or if intensity studies were to be made, a sample was prepared without any container in the following way. A pyrex capillary 20 mm. long of appropriate internal diameter was filled with the powder, which was tamped

with a fine steel wire, and pushed out the end of the capillary a distance of five mm.

For taking high temperature photographs, camera No. III was used with a silica glass "furnace" for heating the sample (Fig. 5). This furnace was made by fusing a one mm. capillary to a tube of bore wide enough to just slip over the centering rod of the camera. In use, a snug fit was

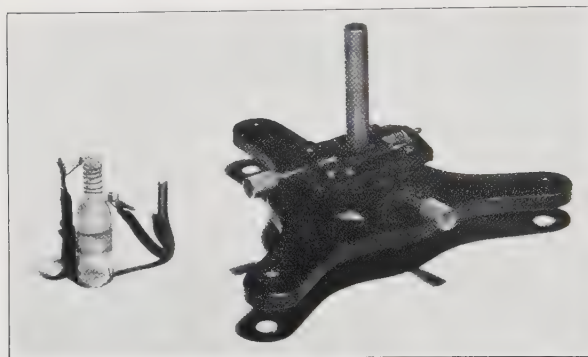


Fig. 5.

made by wrapping the rod with some thin metal foil. This fused silica holder was wrapped with No. 36 ordinary Nichrome wire, which could be used to heat the sample to about 500° . As described before, the powdered sample is packed into the capillary and pushed part way out so as to present a cohering rod of powder to the X-ray beam when the holder is properly mounted.

Temperature calibration was accomplished by placing a fine wire Platinum, Platinum 10% Rhodium thermocouple, beside different parts of the rod of powder.

During the X-ray exposure, no temperature measuring device was used. The power required to maintain the given temperature was determined from the calibration table, and during the exposure the product of current times voltage was maintained constant at this value. For any work where a moderate temperature gradient and moderate inaccuracy are not serious, as was the case here, this offers an inexpensive device which can be quickly and easily prepared and applied to most powder cameras. To obtain much higher temperatures, a more oxidation resistant wire would have to be used. With this small camera the upper temperature limit would then be set by the necessity of protecting the film from heat. Very high temperatures can be attained without this objection by playing

a small gas flame directly on the powder rod, where great temperature accuracy is not required. A pyrex holder will serve instead of silica glass to obtain up to 300° with electrical heating and higher with flame heating.

The films were either measured with a precise millimeter rule, a micro-comparator (Gaertner Scientific Corporation) or a microphotometer (Moll, type A).

All three cameras were calibrated with sodium chloride as standard substance. The samples were of similar thickness (1 mm.) as the silica samples in order to give comparable absorption shifts.

Where greater precision was required, the sample was intimately mixed with sodium chloride and the determination carried through according to the methods given by Wyckoff¹⁾ and H. Ott²⁾.

Chemical Analysis.

There is reported as volatile matter (mostly water), the percentage loss in weight when the air dried sample was ignited to constant weight in a platinum crucible over a Meker burner. There is reported as non volatile impurity, the percentage residue when the sample is evaporated to dryness and ignited at red heat after treatment with 5 ccm. of hydrofluoric acid, to which had been added two drops of concentrated sulfuric acid. The impurities usually present in opals are compounds of iron, aluminum, calcium, magnesium and alkali metals. Therefore, the residues after the latter ignition consist mostly of sulfates and oxides of these elements.

Tabulation of Some Diffraction Measurements.

Table I.

Opals showing high cristobalite lines only.

Calculated θ High Cristobalite $a_0 = 7.078 \text{ \AA}$	Measured θ (corrected)					
	National Museum			Geology Department		
	No. 48095	No. 82566	No. 95752	No. 1	No. 2	No. 3
17.92	17.97	17.70	17.70	17.85	17.85	17.69
21.63 ³⁾	21.58	21.49	21.45	21.73	21.69	21.70
28.28	28.19	28.15	28.15	28.16	28.15	28.12
32.15	32.12	32.15	32.00	32.10	32.18	32.01
34.40	34.21	34.28	34.20	34.20	34.34	34.16
37.95	37.97	37.89	37.85	37.80	37.70	37.74
40.03	39.96	39.98	39.90	39.81	39.90	39.81

1) R. W. G. Wyckoff, Z. Krist. **59**, 55. 1923.

2) H. Ott, Ber. Bayr. Akad. **1924**, 31.

3) Arithmetical mean of two lines which on opal photographs are not resolved.

The largest deviation from calculated θ is 0.25° . Better agreement is not to be expected because the corrections are not rigorously applicable and because of the difficulty in measuring accurately the positions of weak lines on dark backgrounds.

All six patterns gave, upon visual comparison, the same order of relative intensities as the pattern of high cristobalite at 450° C. Conclusions: All six contain high cristobalite; there are no indications of the presence of any other crystalline substance.

The Determination of the Lattice Constant of the High Cristobalite Present in Wood Opal U. S. National Museum No. 48095.

This sample was selected for two reasons. First, it showed only the lines of high cristobalite. Secondly, of the samples analysed for non volatile impurity, it showed a minimum content. The residue (probably as oxide and sulfate) after treatment with hydrofluoric acid-sulfuric acid and ignition to red heat amounted to only 0.40%.

The sample was prepared by thorough grinding of purest sodium chloride with wood opal. The mixture was then packed into a pyrex capillary 0.50 mm. in diameter and pushed partly out of the tube so as to present to the x-ray beam the rod containing only the powder of opal and sodium chloride.

Three sodium chloride and four silica lines were found to be free of overlapping.

All the lines free of overlapping were measured with the comparator to give the values of l used in tables II and III.

Table II.

NaCl lines on comparison photograph.

l (mm.)	true two θ	correction
31.66	31.74	+ .08
66.58	66.30	— .28
84.12	84.10	— .02

Since only three sodium chloride lines were free of overlapping, there were not enough points for the preparation of a useful correction curve. Moreover each of the usable high cristobalite lines fell very close to one of the above three sodium chloride lines. Therefore, the correction for each sodium chloride line was applied to the silica lines very close to it.

Table III.
High cristobalite lines on comparison photograph.

(<i>hkl</i>)	<i>l</i> (mm.)	Correc- tion	two θ	θ	sin θ	a_0	Deviations from mean
220	35.82	+ .08	35.90	17.95	.30849	7.061	— .017
224	64.64	— .28	64.36	32.18	.53263	7.077	— .001
{333 415}	68.84	— .28	68.56	34.28	.56329	7.098	+ .020
435	80.08	— .02	80.06	40.03	.64349	7.077	— .001
					Mean	7.078	$\pm$.010

Wyckoff¹⁾ reported the value $7.12_2 \pm .01$ at 290° and 390° . To determine if this value is consistent with the one found for the opal, it would be necessary to know the coefficient of expansion of high cristobalite from room temperature to 390° C. It is obvious that such measurements are not available. According to Sosman²⁾ "From Braesco's curves it is seen that the dilatation is of the order of 60×10^{-6} at temperatures well above and below the inversion". If this value is accepted, the linear coefficient equals 20×10^{-6} . If this value is used and if it is assumed to be constant through the entire range, the value $a_0 = 7.122$ at a mean temperature of 340° becomes 7.077 at room temperature. Accordingly, there appears to be no inconsistency between Wyckoff's value at 340° and the value for the crystals in opal at room temperature.

The diagram used above shows, definitely, on the photometer curve that the high cristobalite lines are broader than closely situated sodium chloride lines. This indicates colloidal dimensions for the high cristobalite.

Summary of Results with the Opals.

Of nine samples examined, six showed the presence of high cristobalite alone. One showed a mixture of both modifications of cristobalite and two showed a mixture of quartz and cristobalite.

Since the inversion of cristobalite is generally considered to occur promptly and between 150° – 240° ³⁾ it was rather surprising to find high cristobalite existing at room temperature. This raised the question: is the phenomenon due to a temperature or time lag in the inversion or to a lowering of the inversion temperature or to a combination of the three? Opal, U. S. National Museum No. 82566 was immersed in liquid

1) Wyckoff, Am. J. Sci. **9**, 448. 1922. 2) l. c.

3) Sosman, l. c.; R. Weil, C. R. **180**, 1949; **181**, 423. 1925; **182**, 1465; **183**, 753. 1926.

air 40 minutes, removed and immediately photographed by a three hour exposure. The resulting photograph showed only high cristobalite lines as did the original material.

Since Weil¹⁾ reported that treatment with hot concentrated sulfuric acid caused a lowering of the inversion temperature of many of his specimens, the following treatment was tried upon the wood opal sample. It was digested with boiling sulfuric acid one day, washed with water one day, dried at 110° one day, and then photographed at room temperature. No change was observed in the X-ray pattern.

Another experiment consisted in making photographs, at several temperatures, of the sample which showed at room temperature both low and high cristobalite. A photograph made with the sample at 280° showed only high cristobalite lines. A photograph of the sample kept at 170° showed a smaller proportion of low cristobalite than the room temperature photograph. It appears that some of the low cristobalite will not invert till the normal inversion range is reached.

Further, a sample showing high cristobalite lines only, Geology Department No. 4, was heated to 1000°, cooled in air to room temperature and photographed. The resulting pattern was identical with that of the original material.

The only point these experiments establish, is, that evidently the high temperature form of cristobalite present in the opals is surprisingly stable below the well established inversion temperature. It is of interest in this connection to make reference to a note by Greig²⁾ made in answer to our previous report³⁾. Evidently high temperature cristobalite has been observed at room temperature in certain artificial glasses. Such non-inverted crystals appear to adhere strongly and under considerable strains to the glass and this is thought to be the reason for the failure to invert. Undoubtedly the crystals contained in opals are also imbedded in an amorphous material, so that a certain analogy exists.

We quote from the same note "Since the appearance of the letter by Levin and Ott, Dr. E. Posnjak has obtained an X-ray spectrogram, corresponding closely to that given by the high-temperature form of cristobalite, from a translucent ambercolored 'resin opal' from Queretaro, Mexico".

It remains, of course, to establish, under what condition this high temperature cristobalite was formed in opals. At present we have no precise information concerning this point.

1) Weil l. c.

2) J. W. Greig, J. Am. chem. Soc. **54**, 2846. 1932; compare also R. B. Sosman, J. Am. chem. Soc. **54**, 3015. 1932.

3) l. c.

Since the completion of our work, we have obtained a thesis¹⁾ containing some X-ray studies on opals. Crystal diffractions are observed which are identified with quartz. We believe that the measured values of $\sin^2 \theta$ do not agree satisfactorily with those calculated for quartz. In fact in an attempt to identify the lines we find they agree much better with those for low cristobalite. Since no estimates of intensity are made by Dauber we cannot be perfectly sure of this identification.

B. Study of Fused Silica, Hyalite, Geyserite and Silica Gel.

There are in the literature two recent X-ray studies of fused silica. Clark and Amberg²⁾; and Parmalee, Clark and Badger³⁾ reported that calculation by Bragg's law for the points of maximum density of the two observed bands, gave apparent interplanar spacings of 7.1 Å for the strong band and 2.5 Å for the weak band. These workers used molybdenum radiation filtered through a layer of zirconium oxide.

Randall, Rooksby and Cooper⁴⁾ obtained with copper $K\alpha$ -radiation a strong band at 4.33 Å and a faint band at 1.5 Å. Since nothing is said as to the method of obtaining the α -radiation, it may be assumed that the tube outputs were purified only by filtering.

It is known⁵⁾ that when liquids are studied with radiation that is not sufficiently monochromatic, faint peaks may be obscured and spurious peaks introduced. Therefore, a thirty hour exposure was made with copper $K\alpha$ -radiation made practically perfectly monochromatic by a Seemann crystal monochromator.

The sample used was a 0.4 mm. rod drawn from a tube of clear fused silica heated to softness in an oxy-hydrogen torch.

The film was measured on a Moll microphotometer. The spot of light on the film was made 1 mm. wide so as to eliminate the troublesome "grain kinks" obtained if the image of the light source is focused with maximum sharpness upon the film.

The curve (Fig. 6) showed a very strong band with a maximum at θ (corrected for absorption) equal to 40.4 degrees or by Bragg's formula at d equal to 4.27 Å (plus or minus about 0.10 Å). A very flat band occurs also from about θ equal to 29.9° to about θ equal to 43.5° with its maximum at about θ equal to 38.2°. The

1) K. H. Dauber, München 1927/1931.

2) Clark and Amberg, J. Soc. Glass Technology **13**, 290. 1929.

3) Parmalee, Clark and Badger, J. Soc. Glass Technology **13**, 285. 1929.

4) Randall, Rooksby and Cooper, Z. Krist. **75**, 196. 1930.

5) Thibaud and Trillat, Z. Physik **61**, 846. 1930.

corresponding d -values are 1.61 Å, 1.12 Å, and 1.24 Å. Upon visual observation this band seems to consist of three faint bands.

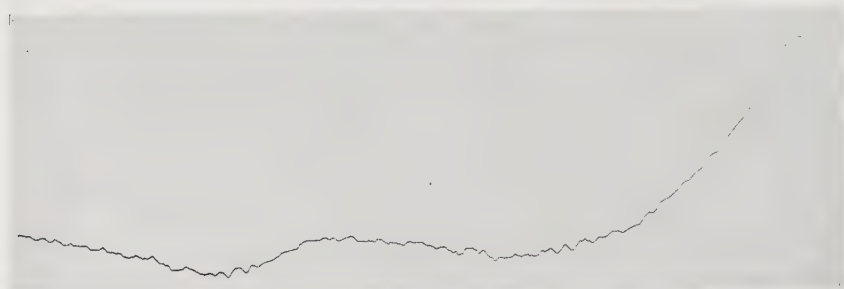


Fig. 6.

It is to be noted that we are in essential agreement with the results of Randall and coworkers.

Randall, Rooksby and Cooper have calculated the shape of the diffraction diagram of low cristobalite if the crystals of the latter have been reduced to 1.5×10^{-7} cm. in length. They write "the sharp peaks are now broad bands and the resultant effect as shown in Fig. 2 (b) is one wide band very similar in shape and size to the observed band for vitreous silica. It is, therefore, very probable that vitreous silica consists largely of crystallites of cristobalite. If the glass consisted of α -quartz crystallites, we should expect a broad band with its maximum at the point marked *A* in Fig. 2 (b). A final possibility is that the glass consists of tridymite crystallites. Tridymite gives lines in very similar positions to those of cristobalite, and the band predicted for tridymite crystallites is of about the same intensity and in the same position as that for cristobalite. The X-ray evidence does not, therefore, allow us to decide whether the glass is made up of one or the other, or both. Tridymite is, however, a comparatively rare mineral and is not easily produced artificially. If fused silica is held at about 1200° C. for a few hours, the devitrification product is invariably cristobalite. It seems, therefore, fairly certain that vitreous silica consists of small crystals of α -cristobalite."

We have two criticisms to make of these conclusions. First, the work by Greig and ourselves on the failure of high cristobalite to invert emphasizes that it is just as likely that cristobalite, if present, would be of the high form. Secondly, calculations by Debye and others show that this type of pattern can be obtained from liquids pictured as not con-

taining crystalline groups of molecules. Zachariasen¹⁾ has also criticized the conclusion of Randall and coworkers.

Results with Silica Gels and Non Crystallized Opals.

This study is based upon five photographs. The first is of the sample of silica glass studied, as explained above, with crystal monochromatized radiation. The remaining four photographs, tabulated below, were obtained under nearly identical tube conditions using radiation purified by filtering through 0.02 mm. of nickel foil.

1. Same sample of silica glass as used above.
2. A commercial silica gel sample.
3. U. S. National Museum No. 94700. Hyalite from Little Switzerland, North Carolina. White translucent crust with surface of globular concretions. Optical examination "No appreciable quantity of doubly refracting material present. Grains are clear. Refractive index 1.418—1.425".
4. Geyserite Y.P. 168 from Dr. Fenner of the Geophysical Laboratory. Sinter from unnamed geyser, edge of Gibbon Meadow, Yellowstone Park.

All of the five samples were photographed without the use of any container.

On the silica glass photograph only the very strong peak at θ equals 10.5 degrees appears distinctly. With samples two, three, and four there appear to the eye on each film three more distinctive bands of which there are only a suggestion on the silica glass film. The measured values of θ for these three bands are 23.5°, 31.5° and 40°; all plus or minus about one degree. It is considered unlikely that these bands are due to the water contained in the pores of these materials, since a photograph of liquid water prepared by Mr. Katzoff in this laboratory showed only one distinctive band at θ equal to 14 degrees. It appears then that there exists greater regularity of atomic arrangement in the silica matrix of these materials than in silica glass itself. It should be emphasized, however, that there are with all four samples no sure indications of the presence of crystalline material.

This study will be continued in this laboratory to determine if one may obtain more explicit conclusions about the constitution of the silica matrix in silica gels and non crystallized opals.

1) W. H. Zachariasen, J. Am. chem. Soc. **54**, 3841. 1932.

Summary.

For the first time the presence of crystalline material (other than quartz) in opals is demonstrated by the X-ray powder method. For most cases the crystals present correspond to high temperature cristobalite (the lattice constant of which was found $a_0 = 7.078 \pm 0.010$ Å.U. at room temperature). This modification of silica has not previously been observed to occur in any natural material at room temperature. (Its presence under corresponding conditions in certain artificial glasses however has been reported by others on the basis of optical examinations.) Other modifications of silica present in certain opals are low temperature cristobalite and quartz.

The diffraction patterns of silica glass and certain silica gels are also discussed.

Acknowledgement.

The authors wish to express their sincere thanks to Dr. E. P. Henderson of the U. S. National Museum, Washington, D. C., for supplying samples and making the optical examinations used in this paper. They are also indebted to Dr. C. N. Fenner and Dr. E. G. Zies of the Geophysical Laboratory, Washington, D. C., as well as to the Geology Department of the Johns Hopkins University for various samples.

Department of Chemistry Johns Hopkins University Baltimore,
Md., U.S.A.

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Observations concerning the structure of interference lines obtained by the powder method¹⁾.

By I. Levin and Emil Ott.

(With 6 figures.)

Möller and Reis²⁾ discuss in two articles the theoretical intensity distribution of diffraction lines obtained by the Debye-Scherrer-Hull method as a function of the cross-section and absorption coefficient of the sample, slit and focus dimension and of the glancing angle. Their calculations show that in the case of a parallel X-ray beam (small effective focus) and a suitable product of absorption coefficient and diameter of the cylindrical sample the resulting diffraction line may appear as a doublet for small glancing angles θ . This effect decreases rapidly with increasing θ due to the disappearance of the inner maximum. The separation of the doublet corresponds approximately to the diameter of the sample. The effect is based on the fact that the rays passing close to the center of the cylinder are absorbed most strongly since they cover a longer path in the sample than any other rays.

When the absorption coefficient becomes large the inner component of the doublet will be too weak to observe. If the absorption coefficient is very small one broad line will be observed. The effect is therefore observed only for a certain range of absorptive power.

The calculations of the second paper show further that the effects mentioned are decreased by use of non-parallel X-rays.

Möller and Reis do not refer to any experimental work demonstrating the calculated doubling. In a review of the textbooks and periodical literature by ourselves we found no references pertinent to this subject.

It appears therefore of importance to report some of our experimental results in this connection.

Several of our recent powder diagrams of high temperature cristobalite showed the existence of such doublets at small glancing angles with such good resolution, that we were at first misled to interpret them as real doublets, which would have required a non-cubic-structure for this substance. Fortunately, we checked this phenomenon with varying thickness of the sample which proved at once that it had nothing to do with the structure of cristobalite itself but was due to some absorption phenomenon. This emphasizes however the importance of this question concerning experimental technique. Additional experiments convinced us that this phenomenon is in qualitative agreement with the afore-mentioned predictions of Möller and Reis.

1) From a thesis on the structure of silica gels (compare I. Levin and E. Ott, *J. Am. chem. Soc.* **54**, 828. 1932 to be submitted by I. Levin in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

2) H. Möller and A. Reis, *Z. physikal. Ch. (A)* **139**, 425. 1928; (B) **2**, 317. 1929. Compare also W. Busse, *Z. Physik* **63**, 227. 1930.

The photographs discussed in the following have been obtained in a cylindrical camera of essentially Scherrer's design, the effective diameter being 57.2 mm. Copper- K_{α} -radiation was used from a metal hot filament tube (Seemann-type). The β -radiation was practically completely absorbed

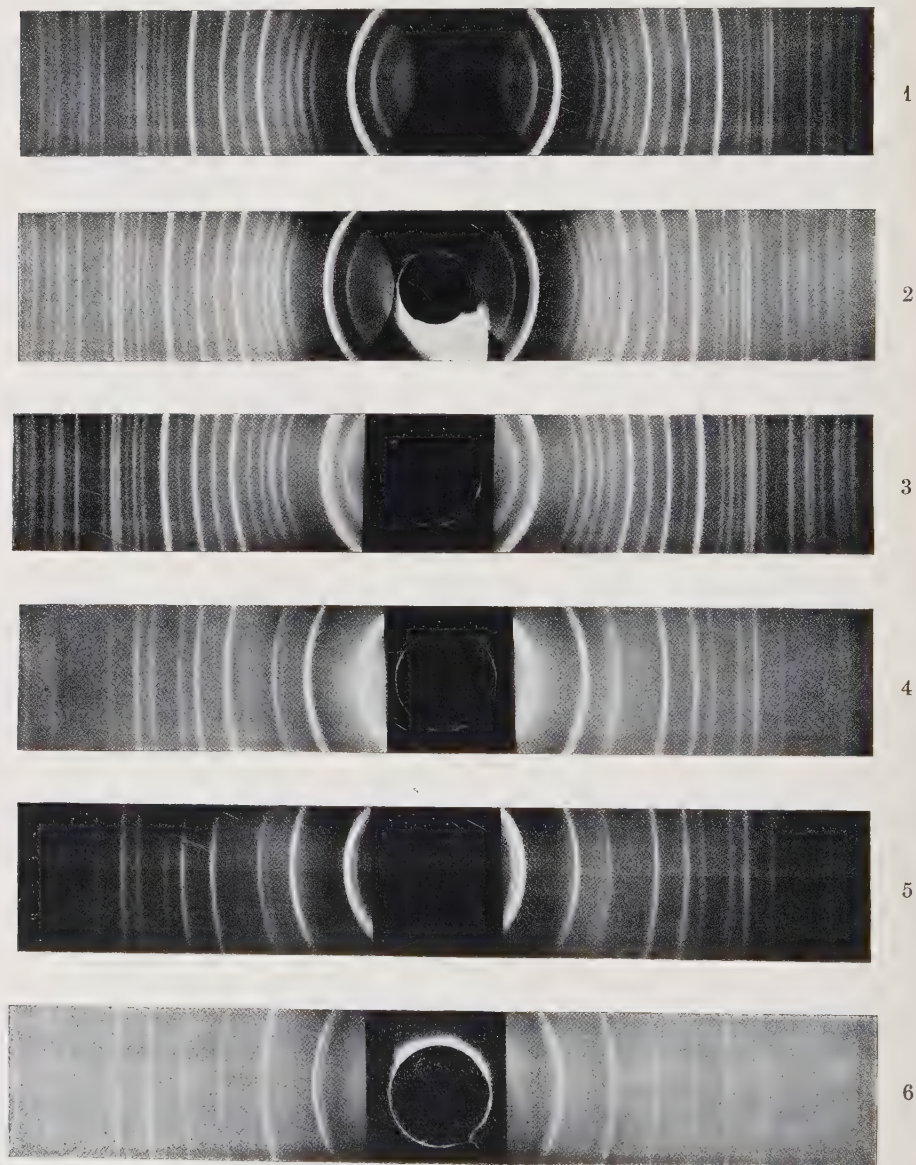


Fig. 4--6.

by 0.02 mm. of nickel foil at the tube window. Also tungsten or any other foreign lines were found sufficiently absent in spectroscopic check-ups.

The photographs 1, 2 and 3 represent powder-diagrams of powdered quartz (sample 3 is a silicified wood, showing quartz lines only). The rods of sample had the following diameters; sample 1, 0.4–0.5 mm.; sample 2, 0.8 mm. and sample 3, 1.0 mm. The samples 1 and 3 were contained in a suitable collodion tube; sample 2 was a perfectly cylindrical pressed rod with no container.

The two inner reflections of photograph 1 (planes (100) and (101) respectively) show only a broadening when compared to other reflections of sample 1. Sample 2 and 3 show definite doublets, the separation of which is in the proper order of magnitude. Also the fact that the inner line of the doublet is of weaker intensity throughout is in agreement with the theory.

The photographs 4 and 5 are obtained from high cristobalite powder, the sample rods having a diameter of 0.5 and 1.0 mm. respectively. Again the first and second innermost reflections (plane (411) and (220)) show the doublet formation in the proper order.

Finally, photograph 6 is obtained from sodium chloride powder contained in a somewhat flattened collodion cylinder having an average inner diameter of 0.7 mm. The reflections of (200) and (220) show definite doublets. It is interesting to note that the weaker inner component of the (200) doublet is far stronger than the (411) reflection.

It seems therefore certain that we have experimentally shown that with $Cu-K_{\alpha}$ -radiation for relatively low absorbent materials, such as silica or sodium chloride powder reflections occurring under small glancing angles up to approximately $\theta = 20^{\circ}$ may be split into definite doublets if the diameter of the sample rod is approximately 0.7 to 1.0 mm. and the average size powder camera is applied. With somewhat smaller diameter of the sample the doublet may merely be indicated by a definite broadening of such reflections. Increased absorption coefficient of the sample with similar rod dimension decreases the effect rapidly.

These facts indicate that the phenomenon is identical with the one predicted by Möller and Reis. The proper separation of the doublets and the limitation to small glancing angles as well as the lower intensity of the inner line of a doublet substantiate this viewpoint.

In conclusion it should be emphasized that a misinterpretation of the doublets above mentioned may lead to serious error in both crystal structure and phase identification work.

Department of Chemistry Johns Hopkins University,
Baltimore, Md., U. S. A.

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Biography.

Isador Levin was born in Baltimore, Md., on Dec. 14, 1909, the son of Mr. and Mrs. Joseph Levin. He attended the primary and secondary schools of Baltimore, graduating in June 1926 from the Forest Park High School. He attended the College of Arts and Sciences of the Johns Hopkins University from Oct. 1926 to June 1928. He entered the Graduate Chemistry Department of the University in October 1928 and was in residence there until the present. During that time he held a Fulton Scholarship 1928—1929, a University Scholarship 1929—1930 and a student assistantship 1930—1931, 1931—1932.
